

## CERTIFICATION

I, Natsuko HIKASA, whose address is Nichimen Building 2F, 2-2, Nakanoshima 2-chome, Kita-ku, Osaka-shi, Osaka, Japan, hereby certify that I am the translator of the attached documents, namely,

Japanese Patent Application No. 2001-5685

that I am familiar with both the Japanese language and the English language, and that the translation is a true and correct translation from the Japanese language to the English language to the best of my knowledge and belief.

This 11th day of November 2003

  
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Natsuko HIKASA

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【Appendix】

【Item】 Specification 1

【Item】 Abstract 1

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【Kind of Document】 Specification

【Title of the Invention】 Golf Ball Printing Method

【Scope of Claims】

【Claim 1】

A method of printing a mark on a surface of a golf ball, comprising a printing process using a two-component curing type ink including a resin having a hydroxyl group, an isocyanate, a coloring agent containing a metal, and a  $\beta$ -diketone.

【Claim 2】

The method according to claim 1, wherein the  $\beta$ -diketone is acetylacetone.

【Claim 3】

The method according to claim 1 or 2, wherein the coloring agent is copper phthalocyanine.

【Claim 4】

The method according to any one of claims 1 to 3, wherein the coloring agent is a metal powder.

【Claim 5】

The method according to any one of claims 1 to 4, wherein the ink has a viscosity adjusted to fall within a range between 3500 cps and 5300 cps.

【Claim 6】

The method according to any one of claims 1 to 5, wherein the printing process comprises the steps of: applying the ink to a pad so that the pattern of the mark is formed on the pad with the ink; and pressing the pad against the surface of the golf ball to transfer the ink forming the pattern of the mark from the pad to the surface of the golf ball.

**【Claim 7】**

A golf ball comprising a mark printed on a surface thereof by a golf ball printing method as recited in any one of claims 1 to 6.

**【Detailed Description of the Invention】****【0001】****【Technical Field of the Invention】**

The present invention relates to methods of printing marks on golf balls with color inks. More particularly, it relates to a golf ball printing method capable of efficient pad printing as well as to golf balls printed with marks by the golf ball printing method.

**【0002】****【Prior Art and the Problem to be Solved】**

In general, a golf ball bears a printed mark of a brand name, play number or the like on a surface thereof. Typical methods of printing such a mark on a golf ball surface include a pad printing process including the steps of: transferring the pattern of a mark formed using an ink contained in an ink fountain to a pad, and pressing the pad against the ball surface to transfer the ink forming the pattern of the mark on the pad to the ball surface; and a transfer printing process including the step of pressing a transfer film having an ink layer forming the pattern of a mark against the ball surface to transfer the mark portion of the film to the ball surface. Since the pad printing process is capable of accommodating to a small lot production, it is employed more widely than the transfer printing process.

**【0003】**

Printing inks for use in golf ball printing are classified into the one-part type which becomes dry through evaporation and the two-component curing type which includes a combination of a base resin and a curing agent.

【0004】

One problem associated with one-component ink is that marks printed with such an ink generally have an insufficient strength, which leads not only to easy peeling or chipping of a printed portion upon iron shot or the like but also to staining of a club face with ink thus peeled off.

【0005】

On the other hand, a two-component curing type ink is advantageous in that: a printed mark formed from cured ink has good durability due to three-dimensional structure of the cured ink; and the ink component such as base resin or curing agent has an affinity to the ball surface to provide a printed mark having high adhesion to the ball surface. However, two-component curing type inks call for control of the rate of curing reaction, because mixing the base resin with curing agent in the ink fountain causes the curing reaction therein to increase viscosity of the ink therein.

【0006】

If the curing reaction proceeds so fast that the ink viscosity becomes too high, a transferring an image formed of ink from an ink fountain to a ball surface through a pad becomes difficult. Particularly, the transferability of the ink to dimpled portions of the ball surface lowers and, hence, a resulting printed mark is likely to suffer from blurring and chipping. For this reason, it is a common practice to control the ink viscosity by appropriately adding a solvent to the ink in accordance as the curing reaction of the ink proceeds in the ink fountain. In the event the ink viscosity control relied only upon the dilution of the ink with a solvent becomes impossible, the ink in the ink fountain is replaced with newly prepared ink.

【0007】

If a sufficient pot life is ensured by the control of the curing reaction of the ink, it is possible to prolong the time interval for ink replacement as well as to decrease variations in the density of the printed mark which may occur depending on the curing reaction.

【0008】

In these years it is a trend that fashionable golf balls are preferred. Printing colorful marks instead of black marks provides such golf balls. Such colorful marks include chromatically colored marks using pigments, and lustrous metallic marks. Recently, golfers tend to prefer marks having metallic luster. To meet such a demand, the art of forming a mark having metallic luster with an ink containing metal powder has been proposed (refer to Japanese Patent Laid-Open Gazette No. HEI 11-114093 for example).

【0009】

In the case of an ink blended with a coloring agent containing a metal powder such as copper powder, brass powder, or copper phthalocyanine, however, such a metal component acts as a catalyst in the curing reaction between the base resin and the curing agent thereby facilitating the curing reaction. Accordingly, two-component curing type ink containing metal powder or metal-containing pigments involve a faster increase in viscosity than two-component curing type ink free of metal powder or metal-containing pigment and hence suffer from a difficulty in viscosity control, which raises the problem of a further shortened pot life. The pad printing using ink having a short pot life requires frequent ink replacements, makes the printing process control cumbersome and raises the cost of producing golf balls.

【0010】

The present invention is made in view of the foregoing circumstances. Accordingly, it is an object of the present invention to provide a golf ball printing method capable of efficient printing of marks on golf balls with colorful or lustrous inks of the two-component curing type ink while ensuring a sufficient pot life. Another object of the present invention is to provide a golf ball bearing a mark printed by this method.

【0011】

According to the present invention, there is provided a method of printing a mark on a surface of a golf ball, including a printing process using of a two-component curing type ink

including a resin having a hydroxyl group, an isocyanate, a coloring agent containing a metal, and a  $\beta$ -diketone.

【0012】

Preferably, the  $\beta$ -diketone is acetylacetone. The coloring agent preferably includes copper phthalocyanine and/or metal powder.

【0013】

Preferably, the ink has a viscosity adjusted to fall within a range between 3500 cps and 5300 cps.

【0014】

In a preferred embodiment of the present invention, the printing process comprises the steps of: applying the ink to a pad so that the pattern of the mark is formed on the pad with the ink; and pressing the pad against the surface of the golf ball to transfer the ink forming the pattern of the mark from the pad to the surface of the golf ball.

【0015】

The present invention also provides a golf ball bearing a mark printed on a surface thereof by one of the golf ball printing method of the present invention.

【0016】

It is to be noted that the term "mark", as used herein, is meant to include letters representing a brand name, an owner's name, or the like, figures, numerals representing a player number or the like, and other indicia.

【0017】

【Embodiment】

The golf ball printing method of the present invention is characterized by using ink including a resin having a hydroxyl group, an isocyanate, a coloring agent containing a metal, and a  $\beta$ -diketone.

【0018】



The ink used in the printing method of the present invention is first described.

【0019】

The ink used in the present invention is two-component curing type ink including a resin having a hydroxyl group and a polyisocyanate as film-forming components, and further including a coloring agent containing a metal, and a  $\beta$ -diketone.

【0020】

The resin having a hydroxyl group serves as the base resin and may be either a resin having a hydroxyl group as a component forming a polymer chain or a resin having a hydroxyl group resulting from ring opening of alcohol, carboxylic acid or epoxy group at the terminal of a polymer chain. Specific examples of such resins include epoxy resin, polyester resin, polyacrylic acid, polyvinyl alcohol, and polyamide resin. Among them, epoxy resin is preferably used because it is excellent in adhesion with a ball surface.

【0021】

The polyisocyanate is contained in the ink as a curing agent for the resin having a hydroxyl group. Specific examples of such polyisocyanates include hexamethylene diisocyanate, xylylene diisocyanate, tetramethylxylylene diisocyanate, tolylene diisocyanate, and hydrogenated diphenyl diisocyanate.

【0022】

The content ratio between the base resin (resin having a hydroxyl group) and the curing agent (polyisocyanate), i.e., curing agent/base resin, is preferably not less than 0.05, more preferably not less than 0.07, much more preferably not less than 0.1. The upper limit of the curing agent/base resin content ratio is preferably 1.0. If the content ratio is less than 0.05, a resulting mark has lowered durability due to the curing agent used insufficiently. If it is more than 1.0, on the other hand, curing proceeds so fast that a sufficient pot life cannot be ensured, resulting in lowered workability.

【0023】

The  $\beta$ -diketone forms a chelate with the coloring agent containing a metal to be described later or surrounds the coloring agent, thereby reducing the frequency of contact

between the film-forming components (the resin having a hydroxyl group and the isocyanate) and the metal-containing coloring agent. Thus, the  $\beta$ -diketone serves to restrain the curing reaction of the film-forming components from being facilitated by the metal-containing coloring agent.

【0024】

The  $\beta$ -diketone preferably has such a low boiling point as to allow easy volatilization thereof. More preferably, the boiling point of the  $\beta$ -diketone ranges between 130°C and 160°C. This is because the  $\beta$ -diketone is contained in the ink in order to inhibit the curing reaction facilitating action of the metal-containing coloring agent and hence will have finished its role after printing of an intended mark on a ball surface with the ink.

【0025】

Examples of such  $\beta$ -diketones include acetylacetone, 3-methyl-2,4-pentadione, 3-ethyl-2,4-pentadione, 3-chloro-acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, and 2,6-dimethyl-3,5-heptadione. Among them, acetylacetone is preferably used.

【0026】

The amount of the  $\beta$ -diketone to be used based on 100 parts by mass of the whole ink composition is preferably not less than 0.1 parts by mass, more preferably not less than 0.5 parts by mass, much more preferably not less than 1.0 part by mass. The ratio between the coloring agent and the  $\beta$ -diketone in content by mass (coloring agent :  $\beta$ -diketone) is preferably in the range of from 10 : 0.1 to 10 : 20, more preferably from 10 : 1 to 10 : 10. If the amount of the  $\beta$ -diketone is less than 0.1 parts by mass or the content ratio of the  $\beta$ -diketone to the coloring agent ( $\beta$ -diketone/coloring agent) is less than 0.1/10, it is insufficient to block the metal contained in the coloring agent. The upper limit of the amount of the  $\beta$ -diketone is preferably 25 parts by mass. In view of the relation between the amount of the  $\beta$ -diketone and the amount of the coloring agent used in the ink, the amount of the  $\beta$ -diketone as large as 25 parts by mass or the content ratio of the  $\beta$ -diketone to the coloring agent ( $\beta$ -diketone/coloring agent) as high as 20/10 is sufficient to block the entire coloring agent and, hence, excess  $\beta$ -diketone contributes only to an increase in the cost of the ink.

【0027】

The coloring agent used in the present invention contains a metal. Examples of usable coloring agents include metal simple substances such as metal powder, metal salts such as red oxide (iron oxide), and metal complexes such as copper phthalocyanine.

【0028】

Copper phthalocyanine or a metal complex of zinc or of a like metal is capable of forming a chelate with the  $\beta$ -diketone and hence assumes a state where the metal thereof is blocked. Thus, the metal is inhibited to serve as a catalyst in the curing reaction. Among metal complex type coloring agents, copper phthalocyanine showing a brilliant blue color is preferably used.

【0029】

A metal simple substance is usually used in the form of metal powder to impart a mark with a metallic tone. Examples of usable metal powders include copper powder, brass powder, a metal powder having a copper/zinc alloy (brass) portion on the surface of each copper particle, gold powder, silver powder, and aluminum powder. Though these metal powders each exhibit a curing reaction facilitating action like metal compounds such as metal complexes, the  $\beta$ -diketone, which is coexistent with such a metal powder as surrounding the metal powder in the ink of the present invention, prevents the metal powder from contacting the film-forming components, i.e., the base resin and the curing agent thereby inhibiting the catalytic action of the metal powder.

【0030】

In the case where the ink needs to transfer from an ink fountain to a pad and from the pad to a ball as in the pad printing process, the viscosity of the ink is critical in the relation between the printability and the appearance and the like of a printed mark. With a view to adjusting the ink viscosity a solvent is preferably contained in the ink. Even if the ink as prepared does not contain any solvent, it is preferred that a solvent be used to dilute the ink having an increased viscosity due to progress of the curing reaction.

【0031】

Any organic solvent that is capable of homogeneously dispersing and dissolving the foregoing resin may be used in the ink of the present invention. Specific examples of such

solvents include aromatic hydrocarbons such as toluene; ester solvents such as methoxybutyl acetate; ether solvents such as methyl ethyl ether; and ketone solvents such as methyl ethyl ketone and cyclohexanone.

【0032】

The viscosity of the ink used in the present invention is preferably within the range of from 3500 to 5300 cps, more preferably from 3500 to 5000 cps, much more preferably from 4000 to 5000 cps. If the ink viscosity is less than 3500 cps, which means that the proportion of the resin relative to the total amount of the ink is insufficient while the proportion of the solvent is excessive, a resulting printed mark is likely to blur. On the other hand, if the ink viscosity is more than 5300 cps, the transferability of the ink to and from a pad becomes lowered due to such a high viscosity and, hence, the occurrence of chipping in a resulting printed mark is likely.

【0033】

Preferably, the ink viscosity falls within the foregoing range not only when the ink has just been prepared (when the base resin and the curing have just been mixed together) but also after lapse of eight hours from the mixing. In the continuous production at an actual plant, change of ink in the middle of the production is cumbersome and brings about disadvantages in terms of productivity and material cost. It is therefore desirable that the ink viscosity be held within the foregoing range even if the viscosity rises while the ink is left for eight hours. It is possible to leave the ink of the present invention for eight hours because the curing reaction inhibitor contained in the ink acts to inhibit a steep rise in viscosity due to progress of the curing reaction.

【0034】

As the need arises, the ink used in the present invention may contain additives such as a matting agent, plasticizer, and filler in addition to the film-forming components, i.e., resin and curing agent, coloring agent and  $\beta$ -diketone.

【0035】

The printing method of the present invention is a method of printing a mark on a ball surface with use of the two-component curing type ink of the composition described above.

【0036】

Though any one of known printing processes such as a process using a transfer foil and a process using a pad may be employed in the present invention, the pad printing process is preferably employed. This is because the pad printing process has a general merit that it is suited to printing onto a curved surface formed with dimples and to a small lot production. Further, the ink used in the present invention is suited to the pad printing process because an increase in the viscosity of the ink can be suppressed to such an extent as not to impede the printing operation and not to affect the appearance of a resulting printed mark by the action of the  $\beta$ -diketone as long as the time period for which the ink is left is not longer than about eight hours.

【0037】

Specifically, the pad printing process employed in the present invention is a process including the steps of: applying the ink contained in an ink fountain to a pad so that the pattern of a mark is formed on the pad with the ink; and pressing the pad against the surface of a golf ball to transfer the ink forming the pattern of the mark from the pad to the surface of the golf ball.

【0038】

Though the curing reaction of the ink in the ink fountain starts proceeding when the base resin and the curing agent are mixed together, the  $\beta$ -diketone acts to inhibit a rapid increase in viscosity due to the curing reaction. Accordingly, it is possible to prevent stringing from occurring between the pad and the ink fountain and between the pad and the ball or a like inconvenience in the process of transferring the ink from the ink fountain to the ball through the pad. Hence, it is possible to avoid chipping of a resulting mark caused by such stringing and formation of an ink mass or the like due to transfer of a stringing portion to the ball surface, whereby a clear-cut mark can be obtained.

【0039】

The pad used in the pad printing process may be a silicone rubber pad conventionally used in pad printing.

【0040】

As the need arises, drying is performed after printing, i.e., after an intended mark has been transferred from the pad to the ball. The drying is achieved at room temperature or by means of hot air at 40°C to 80°C. In the drying process the curing reaction of the ink proceeds as the solvent contained therein volatilizes. If the boiling point of the  $\beta$ -diketone contained in the ink is low, the  $\beta$ -diketone volatilizes to release its blockage against the metal contained in the coloring agent, thereby facilitating the completion of the curing reaction of the ink.

【0041】

The printing method of the present invention is applicable to golf balls of all types without any particular limitation. Examples of such golf balls include: a one-piece golf ball comprising a molded vulcanizate of a butadiene rubber, isoprene rubber or a like rubber; a multi-piece golf ball comprising a core molded from a vulcanized rubber or an elastomer and covered with a cover made from an elastomer, a resin or the like; and a wound-core golf ball comprising a wound core formed by winding rubber thread around a liquid center or a solid center and covered with a cover made from an elastomer, a resin or the like.

【0042】

A golf ball according to the present invention bears a mark printed by the printing method of the present invention. Preferably, a clear paint is applied onto the golf ball so as to coat the entire ball surface including the mark printed thereon, thereby protecting the mark and enhancing the gloss of the entire ball surface.

【0043】

A urethane paint is preferably used as such a clear paint.

【0044】

【Examples】

[Measurement and Evaluation Methods]

#### 1. Viscosity

The viscosity of each ink was measured using a viscometer (VISCOTESTER VT-04 manufactured by RION Co., Ltd.).

【0045】

## 2. Pot life

Each ink just prepared was measured for its viscosity (initial viscosity), thereafter left in a constant temperature chamber set at 40°C for eight hours, and then measured again for its viscosity (viscosity after leaving). The viscosity after leaving was reduced to an index number on the basis of the initial viscosity assumed 1.0, and the pot life of each ink was evaluated based on the index of the viscosity after leaving of the ink according to the following rating criteria:

【0046】

Category “○”:  $1.0 \leq \text{viscosity after leaving} < 1.2$ ;

Category “△”:  $1.2 \leq \text{viscosity after leaving} < 1.4$ ; and

Category “×”:  $1.4 \leq \text{viscosity after leaving}$

【0047】

## 3. Stamp property

A mark was printed on a ball surface by a pad printing process using each ink having been left for eight hours after the preparation thereof. The mark thus printed was evaluated according to the following rating criteria:

Category “○”: a mark with no chipping, blurring or ink mass;

Category “△”: a mark with a chipping, blurring or ink mass having a length of less than 1 mm; and

Category “×”: a mark with a chipping, blurring or ink mass having a length of not less than 1 mm.

【0048】

## 4. Durability of mark

The durability of each mark was evaluated from two viewpoints, i.e., impact resistance

and scuff resistance.

【0049】

a) Impact Resistance

Using a swing robot (manufactured by True Temper Co.) attached with a #1 wood, each ball was hit 200 times repeatedly at a head speed of 45 m/sec. The mark of each ball thus subjected to shots was evaluated as to the degree of peeling according to the following rating criteria:

【0050】

Category “○”: a mark not peeled;

Category “△”: a mark with a peeled portion having a length of less than 2 mm; and

Category “×”: a mark with a peeled portion having a length of more than 2 mm.

【0051】

b) Scuff Resistance

Using the above robot attached with a sand wedge, a bunker shot was performed 50 times. Each mark thus subjected to bunker shots was evaluated as to the degree of peeling according to the following rating criteria:

【0052】

Category “○”: a mark with no chipping or scuffing;

Category “△”: a mark with a chipping or scuffing having a length of less than 2 mm;

and

Category “×”: a mark with a chipping or scuffing having a length of more than 2 mm.

【0053】

[Manufacture of Golf Ball]



## 1. Preparation of Ink

Inks Nos. 1 to 9 having respective compositions shown in Table 1 were prepared.

【0054】

Copper phthalocyanine blue or brass powder was used as a coloring agent. Acetylacetone produced by Daicel Chemical Ind. was used as a  $\beta$ -diketone, while an aromatic hydrocarbon used as a solvent.

【0055】

Inks Nos. 1 to 5 each containing acetylacetone were examples of the present invention, while other inks were comparative examples out of the scope of the present invention.

【0056】

## 2. Printing of Mark

The surface of a two-piece golf ball including a rubber core and an ionomer cover covering the core was subjected to a sandblasting treatment, and then printed with a mark by pad printing (using a silicone rubber pad) with use of each of inks Nos. 1 to 9 thus prepared. After the printing, a clear paint was applied onto each golf ball so as to cover the entire golf ball surface including the mark thus printed thereon.

【0057】

In this case, a urethane paint was used as the clear paint.

[0058]

Table 1

		1	2	3	4	5	6	7	8	9
Ink composition	Epoxy resin	2 4	2 4	2 4	2 4	2 4	2 4	2 4	2 4	2 5
	Isocyanate	2	2	2	2	2	2	5	2	—
	Phthalocyanine blue	1 0	1 0	1 0	1 0	—	1 0	1 0	—	1 0
	Brass powder	—	—	—	—	1 0	—	—	1 0	—
	Matting agent	1 4	1 4	1 4	1 4	1 4	1 4	1 3	1 4	1 4
	Acetylacetone	5	0.05	0.1	10	5	—	—	—	—
	Aromatic hydrocarbon	4 5	49.95	49.9	40	45	50	48	50	51
Evaluation	Initial viscosity	4000	4000	4000	4000	4300	4000	4200	4300	4100
	Viscosity after leaving	4500	4800	4600	4400	5000	5500	7500	8000	4500
	Pot life	○	△	○	○	○	△	×	×	○
	Printability	○	○	○	○	○	△	×	×	○
	Impact resistance	○	○	○	○	○	○	○	○	×
	Scuff resistance	○	○	○	○	○	○	○	○	×

【0059】

Inks Nos. 7 and 8 each exhibited a large increase in viscosity due to phthalocyanine blue or brass powder acting to facilitate the curing reaction. They were judged to have a difficulty in ensuring a pot life of eight hours when the relation between their largely increased viscosity and their inferior stamp property were taken into consideration.

【0060】

Ink No. 6 had a lowered initial viscosity as compared with inks Nos. 7 and 8 by adjustment of the amounts of the curing agent and solvent used. However, the viscosity of this ink after having been left for eight hours exceeded 5300 cps due to the absence of acetylacetone and, accordingly, the stamp property of ink No. 6 was inferior.

【0061】

Ink No. 9 did not contain any curing agent. This ink did not exhibit a substantial increase in viscosity even in the absence of acetylacetone and hence exhibited satisfactory pot life and stamp property. However, ink No. 9 could not yield a mark having satisfactory durability. Though the viscosity of ink No. 9 increased to some extent despite the absence of any curing agent, an increase in viscosity to such an extent is possible to occur due to volatilization of the solvent used.

【0062】

Inks Nos. 1 to 5 each containing phthalocyanine blue or brass powder together with acetylacetone could suppress an increase in viscosity to a value less than 1.2 times as large as the initial viscosity and hence ensured a satisfactory pot life. Among them, ink No. 2 containing acetylacetone in an amount as small as 0.05 parts by mass exhibited somewhat inferior stamp property because the blocking effect of acetylacetone was insufficient.

【0063】

【Effect】

The golf ball printing ink of the present invention is a two-component curing type ink that is capable of yielding a mark having superior durability. Since an increase in the viscosity of the ink due to progress of the curing reaction of the ink is inhibited, the ink is capable of ensuring a sufficient pot life.

【0064】

The golf ball according to the present invention bears a mark printed with the ink of the present invention exhibiting the foregoing effects as well as good printability. In the manufacture of this golf ball it is possible to use the ink prepared in the beginning of a production run in the morning until the end of the production run in the evening of the same date. This is convenient in production control.

【Kind of Document】 Abstract

【Summary】

【Object】 To provide an improved golf ball printing method which is capable of efficient printing of marks on golf balls with colorful or lustrous inks of the two-component curing type while ensuring a sufficient pot life, as well as a golf ball bearing a mark printed by this method.

【Means for Solving the Object】 A method for printing a mark on surface of a ball, the method using a two-component curing type ink comprising a resin having a hydroxyl group, an isocyanate, a coloring agent containing a metal, and a  $\beta$ -diketone. In an embodiment the  $\beta$ -diketone is acetylacetone. In another embodiment the coloring agent includes copper phthalocyanine and/or metal powder.

【Selected Figure】 none